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ORIGINAL ARTICLE

Synthesis, characterization and complexation studies of *bis*-oxy biphenyl based novel diamides

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KEYWORDS

Diamides;
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Abstract A series of *bis*-oxy biphenyl based diamides have been synthesized and characterized from spectral and XRD data. All the diamides form charge-transfer (CT) complex with 7,7,8,8-tetracyanoquinodimethane (TCNQ).

1. Introduction

In the past decade, design and synthesis of hydrogen-bonding fluoro receptor for selective sensing of anions were the focus of interest for chemists due to the important roles of anions in many biological and chemical systems (Steed, 2006; Martinez-Manez and Sancenon, 2003; Caltagirone and Gale, 2009; Gale et al., 2008; Sessler et al., 2007). The development of synthetic receptors for anions is of considerable interest because of their potential biomedical and environmental applications (O'Leary et al., 2001; Barwell et al., 2009; and Barwell and Davis, 2011). Biphenyl based pyridinium diamide is a simple synthetic receptor for selective recognition of dihydrogen phosphate (Ghosh et al., 2009). Diamides of dicarboxylic acids like diglycolic acids, dipicolinic and 2,2′-dipyridyl-6,6′dicarboxylic acids are more powerful extractants for actinide and lanthanide recovery (Alyapyshev et al., 2010). Diamides prepared from reaction of 2-amino-6-methylpyridine, 2,6-diaminopyridine with isophthalic acid and their self-assembling properties through hydrogen bonding are reported (Mazik et al., 1999). The last four decades has resulted in a variety of new synthetic progress, new techniques and coupling reagents such as HATU and PyBOP (Przemysaw Reszka et al., 2008). Study of host–guest complexes using guests of biological interest to mimic the function of natural receptors of diamides derived from isophthalic acid has been reported recently (Claramunt et al., 2005).

Diamides of phthalic acid can be used as a new structural class of highly potent insecticides especially against lepidopteron insects (Feng et al., 2010a,b). The diamides prepared from 2-phenylimidazopyridines were effective in animal models of asthma, cancer, inflammation and infectives (Banie et al., 2007). Biaryl diamides exhibited as a potent melanin concentrating hormone receptor 1 antagonist (Palani et al., 2005). The biphenyl diamides are a novel series of p38 MAP kinase inhibitors (Angell et al., 2008a,2008b). Synthesis of new chiral receptors containing (S)-BINOL and thiourea units and their enantioselective recognition ability for chiral carboxylate

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anions has been recently reported (Hu et al., 2009). Interaction between an electron donor and an electron acceptor moiety in amides could result in the formation of either a charge transfer (CT) complex or л-л stacking interactions (Hunter and Purvis, 1992; Rajakumar and Padmanabhan, 2011; Szumna and Jurczak, 2001; Katoono et al., 2005; Bru et al., 2005; Inoue et al., 1997; Inoue et al., 1998; Ngu-schwemlein et al., 2008; Collins et al., 1991). Such amides are in general called as self-complementary amides. Developing amide systems, which exhibit CT complexation, metal complexation (Singh and Chaudhary, 2004; Katagiri et al., 2009; Shinubu et al., 2002) and biological activity (Ranganathan et al., 2000; Li et al., 1996) is an ever interesting and challenging problem. Hence, it is of interest to synthesize and study the CT complexation, metal complexation properties, and biological activity of novel amides. Herein, we report the synthesis of amides **1**–**14** (Fig. 1) and their charge transfer complexation studies with 7,7,8,8-tetracyanoquinodimethane (TCNQ).

2. Experimental

2.1. General

All the reagents and solvents employed were of the best grade available and were used without further purification. The melting points were determined using a Mettler Toledo melting point apparatus by the open capillary tube method and were uncorrected. Spectroscopic data were recorded by the following instruments: UV/ Vis: Shimadzu 2550 spectrophotometer. IR: Perkin-Elmer series 2000 FTIR spectrophotometer. NMR: Bruker Avance 400 MHz. Mass: ESI – PerkinElmer Sciex, API 3000 mass spectrometer and FAB-mass spectra Jeol SX 102/ DA-6000 mass spectrometer. The elemental analysis for the compounds was carried out using the Elementar Vario EL III elemental analyzer (SIPRA LABS Ltd., Hyderabad, India). Pre-coated silica gel plates from Merck were used for TLC. Column chromatography was carried out using silica gel (100–200 mesh) purchased from ACME.

2.2. General procedure for the synthesis of diamides

To a solution of diacid (1.0 mmol) in dry DMF (10 mL), (*O*-Benzotriazole-*N*,*N*,*N*′,*N*′-tetramethyl-uronium-hexafluoro-phosphate) HBTU (2.5 mmol), diisopropylethylamine (2.2 mmol) were added and stirred for 30 min. Amine (3.0 mmol) was added to the reaction mixture and stirred for further 3 h. The progress of the reaction was monitored by HPLC. The reaction mixture was poured into ice water and filtered. The solid was washed with water followed by cold ethanol and dried under vacuum. The crude product was purified by column chromatography (SiO_2).

2.3. HPLC analysis

HPLC analysis was carried out on a Waters Alliance 2695 separations module with photodiode array detector (Waters, 2996). The LC column was a YMC pack ODS A (150 mm × 4.6 mm, 5 μm). Two mobile phases A (consisted of water with 0.1% ortho phosphoric acid) and B (acetonitrile) were used at flow rate of 1.0 mL/min. A gradient was used, starting at 90% A, changing to 70% A linearly in 20 min.

2.3.1. 2,2′-(biphenyl-2,2′-diybis(oxy)bis(N-phenylacetamide) (1)

Yield 65%; mp 174 °C; IR (KBr, cm^{-1}) 1683; ^1H NMR (400 MHz, DMSO-d_6) δ 9.65 (s, 2H, NH), 7.48 (d, 4H, J = 8.04 Hz), 7.34–7.38 (m, 4H), 7.26 (t, 4H, J = 7.6 Hz), 7.04–7.09 (m, 6H), 4.68 (s, 4H, CH_2O); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.5, 155.2, 138.1, 131.5, 128.8, 127.4, 123.7, 121.2, 119.4, 112.8, 67.7; MS (ES) *m*/*z*: 453.1

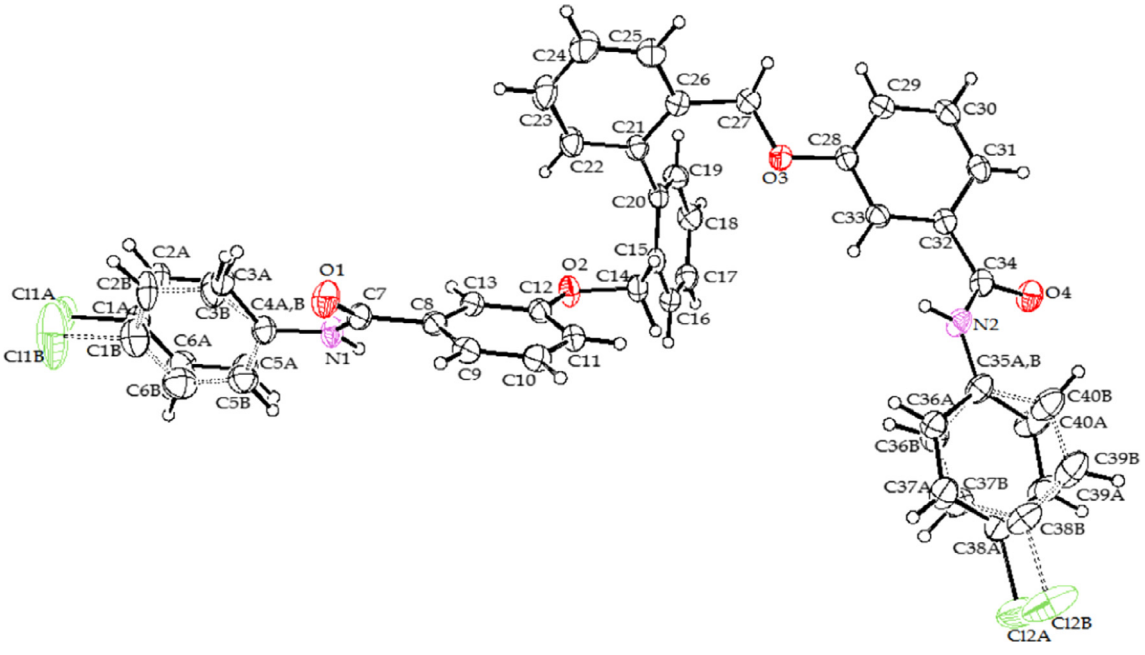
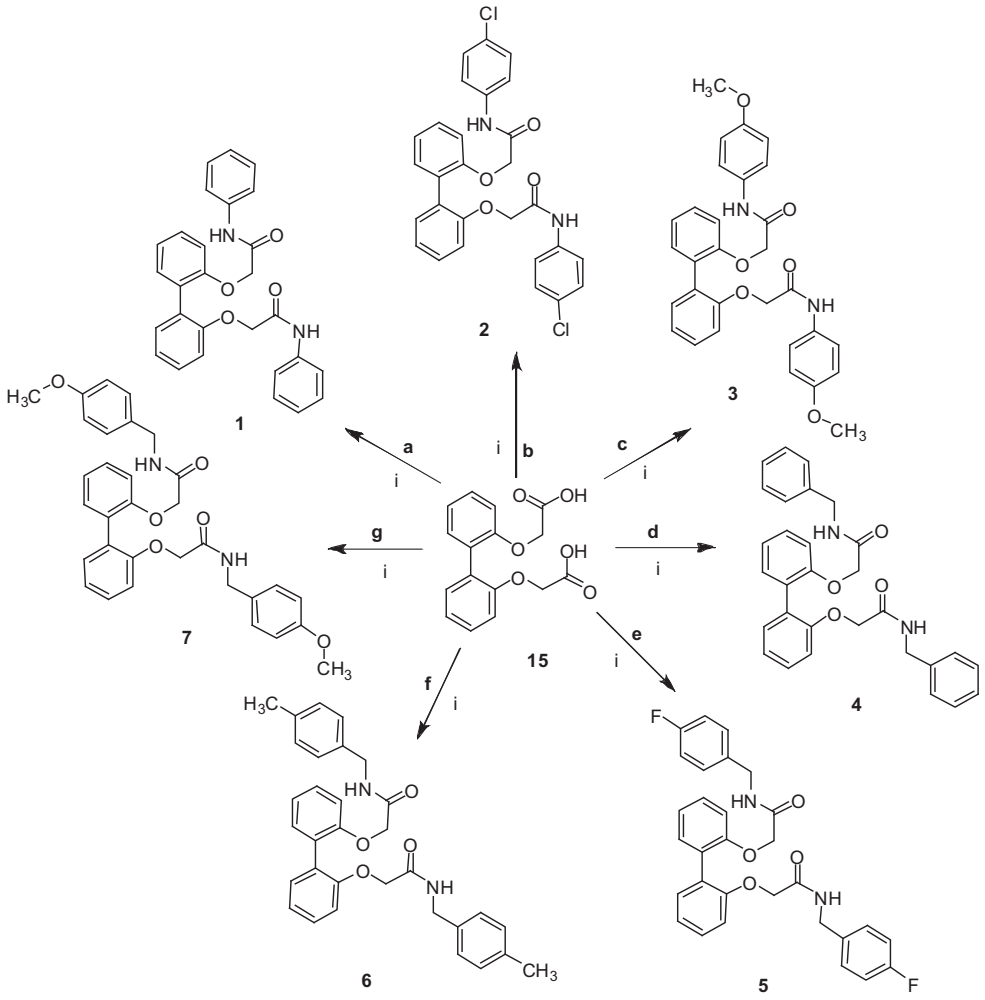


Figure 1 ORTEP diagram of diamide **9**.



Scheme 1 Reagents and conditions: (i) HBTU, DMF, rt, 3 h, **1** (65%), **2** (60%), **3** (70%), **4** (65%), **5** (68%), **6** (75%) and **7** (72%). **Amine**: (a) Aniline, (b) 4-Chloroaniline, (c) 4-methoxyaniline, (d) Benzyl amine, (e) 4-Flurobenzyl amine, (f) 4-methylbenzyl amine and (g) 4-methoxybenzyl amine.

$[M+H]^+$; Elemental Anal. Calc. for. $C_{28}H_{24}N_2O_4$ C, 74.32; H, 5.35; N, 6.19%; Found: C, 75.12; H, 5.41; N, 6.25.

*2.3.2. 2,2′-(biphenyl-2,2′-diybis(oxy)bis(N-(4-chlorophenyl)acetamide) (**2**)*

Yield 60%; mp 194 °C; IR (KBr, cm^{-1}) 1698; ^1H NMR (400 MHz, DMSO-d_6) δ 9.84 (s, 2H, NH), 7.49 (d, 4H, J = 8.9 Hz), 7.31–7.37 (m, 8H), 7.04–7.08 (m, 4H), 4.67 (s, 4H, CH_2O); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.8, 155.2, 137.1, 131.5, 128.8, 128.6, 127.4, 127.3, 121.2, 120.9, 112.9, 67.7; MS (ES) m/z: 521.1 $[M+H]^+$; Elemental Anal. Calc. for. $C_{28}H_{22}Cl_2N_2O_4$ C, 64.50; H, 4.25; N, 5.37%; Found: C, 63.85; H, 4.17; N, 5.46.

*2.3.3. 2,2′-(biphenyl-2,2′-diybis(oxy)bis(N-(4-methoxyphenyl)acetamide) (**3**)*

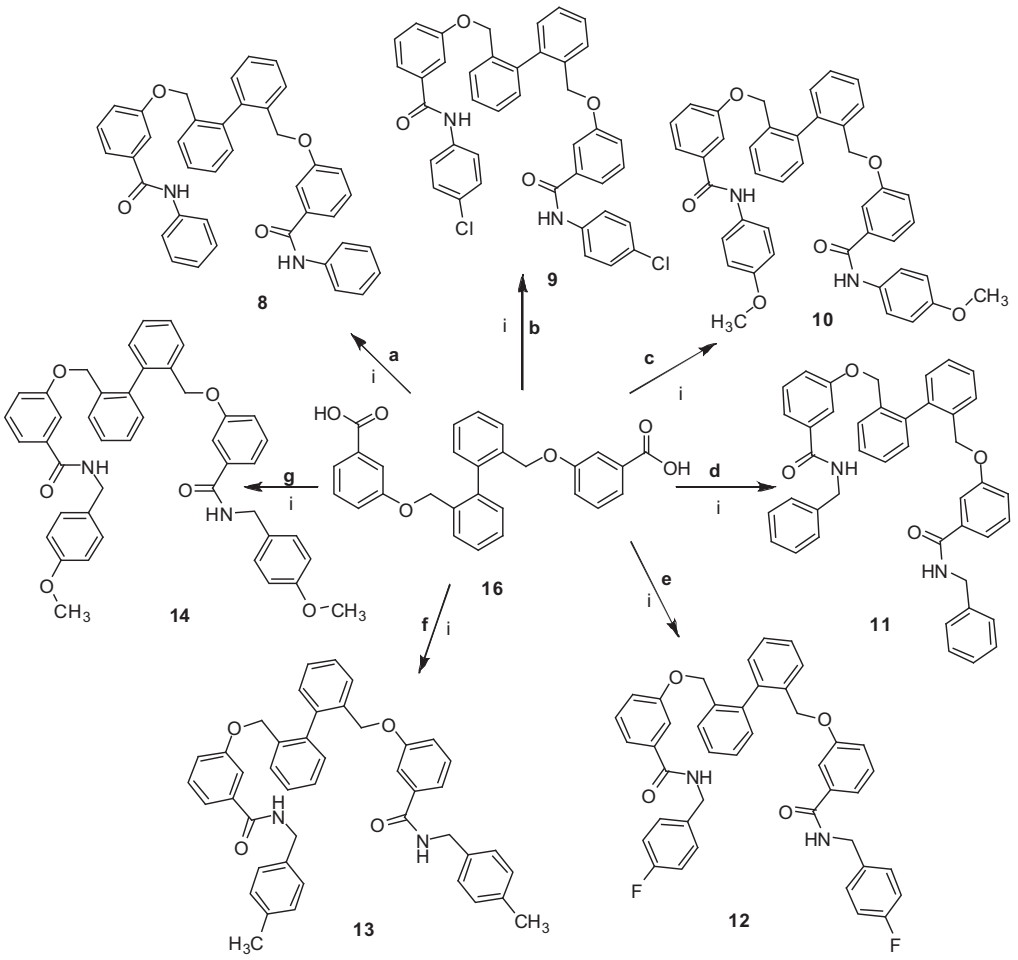
Yield 60%; mp 197 °C; IR (KBr, cm^{-1}) 1688; ^1H NMR (400 MHz, DMSO-d_6) δ 9.49 (s, 2H, NH), 7.34–7.39(m, 8H), 7.05–7.08 (m, 4H), 6.83 (d, 4H, J = 9.0 Hz), 4.63 (s, 4H, CH_2O), 3.71 (s, 6H, CH_3O); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.1, 155.4, 131.5, 131.2, 128.8, 127.5, 121.2, 121.1, 113.9, 112.8, 67.7, 55.2; MS (ES) m/z: 513.1 $[M+H]^+$; Elemental Anal. Calc. for. $C_{30}H_{28}N_2O_6$ C, 70.30; H, 5.51; N, 5.47%; Found: C, 70.95; H, 5.05; N, 5.05.

*2.3.4. 2,2′-(biphenyl-2,2′-diybis(oxy)bis(N-acetamide) (**4**)*

Yield 65%; mp 151 °C; IR (KBr, cm^{-1}) 1669; ^1H NMR (400 MHz, DMSO-d_6) δ 8.15 (t, 2H, J = 5.9 Hz, NH), 7.20–7.32 (m, 10H), 7.12 (d, 4H, J = 6.9 Hz), 6.98 (t, 2H, J = 7.4 Hz), 6.92 (d, 2H, J = 8.2 Hz), 4.45 (s, 4H, CH_2O), 4.25 (d, 4H, J = 5.9 Hz, CH_2N), ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.9, 155.20, 138.9, 131.3, 128.7, 128.2, 127.5, 127.2, 126.8, 121.1, 112.5, 67.5, 41.8; MS (ES) m/z: 481.1 $[M+H]^+$; Elemental Anal. Calc. for. $C_{30}H_{28}N_2O_4$ C, 74.98; H, 5.87; N, 5.83%; Found: C, 74.75; H, 5.56; N, 5.98.

*2.3.5. 2,2′-(biphenyl-2,2′-diylbis(oxy))bis(N-(4-flurobenzyl)acetamide) (**5**)*

Yield 68%; mp 151 °C; IR (KBr, cm^{-1}) 1669; ^1H NMR (400 MHz, DMSO-d_6) δ 8.20 (t, 2H, J = 5.9 Hz, NH), 7.29–7.33 (m, 2H), 7.22 (dd, 2H, J = 7.4 & 1.4 Hz), 7.15–7.18 (m, 4H), 7.05–7.09 (m, 4H), 6.99 (t, 2H, J = 7.4 Hz), 6.91 (d, 2H, J = 8.2 Hz), 4.46 (s, 4H, CH_2O),4.23 (d,4H, J = 5.9 Hz, CH_2N); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.9, 162.4,



Scheme 2 Reagents and conditions: (i) HBTU, DMF, rt, 3 h, **8** (65%), **9** (70%), **10** (65%), **11** (65%), **12** (66%), **13** (74%) and **14** (62%). **Amine**: (a) Aniline, (b) 4-Chloroaniline, (c) 4-methoxyaniline, (d) Benzyl amine, (e) 4-Flurobenzyl amine, (f) 4-methylbenzyl amine and (g) 4-methoxybenzyl amine.

159.9, 155.2, 135.2, 131.3, 129.2, 129.1, 128.7, 127.5, 121.1, 115.0, 114.8, 112.5, 67.5, 41.1; MS (ES) *m/z*: 517.1 $[M+H]^+$ Elemental Anal. Calc. for. $C_{30}H_{26}F_2N_2O_4$: C, 69.76; H, 5.07; N, 5.42%; Found: C, 69.31; H, 5.30; N, 5.36.

*2.3.6. 2,2′-(biphenyl-2,2′-diybis(oxy)bis(N-(4-methylbenzyl)acetamide) (**6**)*

Yield 75%; mp 175 °C; IR (KBr, cm^{-1}) 1669; ^1H NMR (400 MHz, DMSO-d_6) δ 8.08 (t, 2H, J = 5.9 Hz, NH), 7.28 (t, 2H, J = 8.84 Hz), 7.22 (dd, 2H, J = 7.4 & 1.4 Hz), 7.06–7.08 (m, 4H), 6.98–7.02 (m, 6H), 6.91 (d, 2H, J = 8.3 Hz), 4.43 (s, 4H, CH_2O), 4.20 (d, 4H, J = 5.9 Hz, CH_2N), 2.26 (s, 6H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.8, 155.2, 135.9, 131.3, 128.8, 128.7, 127.5, 121.2, 121.1, 112.5, 67.4, 41.6, 20.7; MS (ES) *m/z*: 509.2 $[M+H]^+$; Elemental Anal. Calc. for. $C_{32}H_{32}N_2O_4$: C, 75.57; H, 6.34; N, 5.51%; Found: C, 75.21; H, 6.67; N, 5.90%.

2.3.7. 2,2′-(biphenyl-2,2′-diylbis(oxy))bis(N-(4-methoxybenzyl)acetamide) (7)

Yield 72%; mp 133 °C; IR (KBr, cm^{-1}) 1664; ^1H NMR (400 MHz, DMSO-d_6) δ 8.03 (t, 2H, J = 5.9 Hz, NH), 7.28 (t, 2H, J = 9.2 Hz), 7.21 (dd, 2H, J = 8.2 &1.7 Hz), 7.04 (d, 4H, J = 8.6 Hz), 6.98 (t, 2H, J = 7.4 Hz), 6.90 (d, 2H, J = 8.3 Hz), 6.80–6.83 (m, 4H), 4.42 (s, 4H, CH_2O), 4.18 (d, 4H, J = 5.9 Hz, CH_2N), 3.72 (s, 6H, CH_3O); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.7, 155.2, 131.2, 130.9, 128.7, 128.6, 127.5, 121.1, 113.6, 112.5, 67.5, 55.0, 41.3; MS (ES) *m/z*: 541.2 $[M+H]^+$ Elemental Anal. Calc. for. $C_{32}H_{32}N_2O_6$: C, 71.09; H, 5.97; N, 5.18%; Found: C, 71.21; H, 5.70; N, 5.36%.

*2.3.8. 3,3′-(biphenyl-2,2′-diylbis(methylene))bis(oxy)bis(N-phenylbenzamide) (**8**)*

Yield 65%; mp 90 °C; IR (KBr, cm^{-1}) 1652; ^1H NMR (400 MHz, DMSO-d_6) δ 10.18 (s, 2H, NH), 7.74 (d, 4H, J = 8 Hz), 7.61 (d, 2H, J = 6.9 Hz), 7.48 (d, 2H, J = 7.6 Hz), 7.39–7.44 (m, 6H), 7.32–7.44 (m, 8H), 7.08 (t, 2H, J = 7.3 Hz), 7.02 (dd, 2H, J = 8.2 & 1.7 Hz), 4.86 (ABq, 4H J = 11.4 Hz, CH_2O); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.1, 158.1, 139.5, 139.1, 136.3, 134.3, 129.9, 129.5, 129.2, 128.6, 128.0, 127.9, 123.7, 120.4, 120.1, 117.8, 113.6, 67.8; MS (ES) *m/z*: 605.2 $[M+H]^+$; Elemental Anal. Calc. for. $C_{40}H_{32}N_2O_4$: C, 79.45; H, 5.33; N, 4.63%; Found: C, 79.85; H, 5.59; N, 4.85%.

Table 1 Crystal data for diamide **9**.

Crystal	
Empirical formula	$C_{40}H_{30}Cl_2N_2O_4$
Formula mass	673.56
Color	Block colorless
Crystal dimensions (mm)	$0.30 \times 0.25 \times 0.20$
Crystal system	Triclinic
Space group	P−1 (No. 2)
Z	2
a (Å)	9.4761 (2)
b (Å	11.9967 (3)
c (Å)	15.9238 (4)
α (°)	75.9440 (10)
β (°)	86.1630 (10)
γ (°)	69.3680 (10)
Temperature (°K)	296 (2)
Volume (Å^3)	1643.07 (7)
D_{calcd} (mg m^{-3})	1.361
Absorption coeff. (μ, mm^{-1})	0.240
Absorption correction	Multi-scan (SADABS)
Radiation	Mo Kα (0.71073)
θ range for data collection (°)	$2.3 \leqslant \theta \leqslant 24.7$
Observed reflections	33,102
CCDC No. (Supplementary data)	890615

Table 2 λ_{max} for diamides and TCNQ complex of diamides **1–14**.

Amide	λ_{max} (nm) of the amide	λ_{max} (nm) of TCNQ complex
1	240	742
2	247	742
3	248	742
4	275	742
5	232	742
6	272	743
7	276	743
8	264	742
9	286	743
10	286	744
11	287	742
12	271	744
13	267	743
14	275	743

*2.3.9. 3,3′-(biphenyl-2,2′-diylbis(methylene))bis(oxy) bis(N-(4-chlorophenyl)benzamide) (**9**)*

Yield 70%; mp 150 °C; IR (KBr, cm^{-1}) 1652; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.29 (s, 2H, NH), 7.78 (d, 4H, J = 8.8 Hz), 7.61 (d, 2H, J = 6.7 Hz), 7.48 (d, 2H, J = 7.6 Hz), 7.42–7.44 (m, 4H), 7.38–7.40 (m, 6H), 7.31 (t, 4H, J = 7.5 Hz), 7.02 (d, 2H, J = 8.0 Hz), 4.86 (ABq, 4H J = 11.5 Hz, CH$_2$O); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 165.2, 158.1, 139.5, 138.1, 136.0, 134.3, 129.8, 129.5, 129.2, 128.5, 128.0, 127.9, 127.3, 121.9, 120.1, 117.9, 113.7, 67.9; MS (ES) m/z: 673.2 [M + H]$^+$; Elemental Anal. Calc. for. $C_{40}H_{30}Cl_2N_2O_4$: C, 71.85; H, 4.10; N, 4.39%; Found: C, 71.85; H, 4.10; N, 4.39%.

*2.3.10. 3,3′-(biphenyl-2,2′-diylbis(methylene))bis(oxy) bis(N-(4-methoxyphenyl)benzamide) (**10**)*

Yield 70%; mp 70 °C; IR (KBr, cm^{-1}) 1646; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 10.05 (s, 2H, NH), 7.63–7.65 (m, 4H), 7.60–7.63 (m, 2H), 7.47 (d, 2H, J = 7.7 Hz), 7.37–7.45 (m, 6H), 7.31 (t, 4H, J = 8 Hz), 6.99–7.02 (m, 2H), 6.89–6.93(m, 4H), 4.85(ABq, 4H J = 11.4 Hz, CH$_2$O), 3.74 (s, 6H J = 7.6, CH$_3$O); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 164.7, 158.1, 155.6, 139.5, 136.9, 134.3, 132.1, 129.8, 129.5, 129.2, 128.0, 127.9, 122.0, 119.9, 117.7, 113.7, 113.5, 67.8, 55.2; MS (ES) m/z: 665.2 [M + H]$^+$: Elemental Anal. Calc. for. $C_{42}H_{36}N_2O_6$: C, 75.89; H, 5.46; N, 4.21%; Found: C, 75.62; H, 5.59; N, 4.65%.

*2.3.11. 3,3′-(biphenyl-2,2′-diylbis(methylene))bis(oxy) bis(N-(4-methoxyphenyl)benzamide) (**11**)*

Yield 65%; mp 70 °C; IR (KBr, cm^{-1}) 1639; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 8.98 (t, 2H, J = 5.72 Hz, NH), 7.58(d, 2H, J = 6.9 Hz), 7.43 (d, 2H, J = 7.7 Hz), 7.37–7.40 (m, 6H), 7.28–7.31 (m, 11H), 7.22–7.26 (m, 3H), 6.94 (d, 2H, J = 8.0 Hz), 4.81 (ABq, 4H J = 11.4 Hz, CH$_2$O), 4.45–4.46, (d, 4H J = 5.8, CH$_2$N); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 165.8, 158.1, 139.6, 139.5, 135.7, 134.3, 129.8, 129.4, 129.2, 128.3, 127.9, 127.8, 127.2, 126.7, 119.6, 117.6, 113.2, 67.8, 42.6; MS (ES) m/z: 633.3 [M + H]$^+$; Elemental Anal. Calc. for. $C_{42}H_{36}N_2O_4$: C, 79.72; H, 5.73; N, 4.43%; Found: C, 79.92; H, 5.59; N, 4.12%.

*2.3.12. 3,3′-(biphenyl-2,2′-diylbis(methylene))bis(oxy) bis(N-(4-flurobenzyl)benzamide) (**12**)*

Yield 66%; mp 198 °C; IR (KBr, cm^{-1}) 1641; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 8.98 (t, 2H, J = 5.9 Hz, NH),

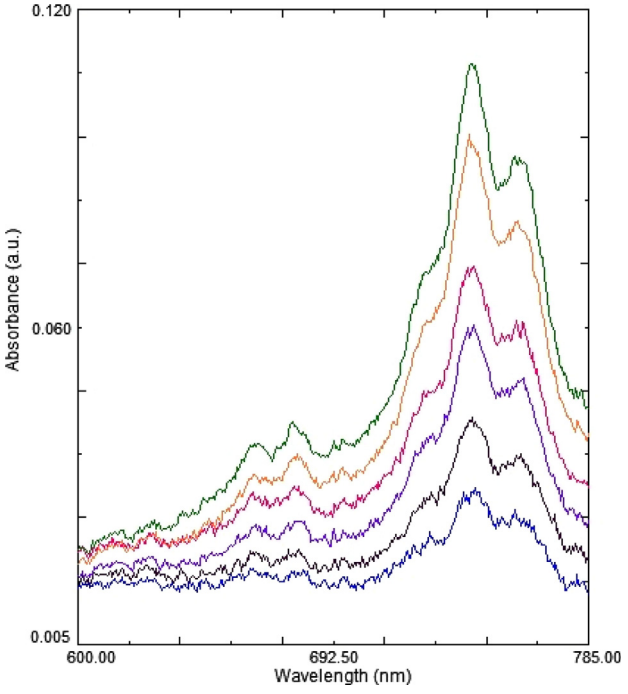


Figure 2a Charge transfer complexation behavior of diamide **9** with variable concentrations of TCNQ (1 mL to 6 mL).

Table 3 Benesi–Hildebrand treatment data of the CT complex formed between the amide, **9** and TCNQ.

Conc. of guest, [×] (M)	Absorbance, A	[Y]/A(M)	1/[X] (M^{-1})
4.9×10^{-6}	0.016	0.001263	204,081
9.8×10^{-6}	0.028	0.000721	102,040
14.7×10^{-6}	0.045	0.000449	68,027
19.6×10^{-6}	0.057	0.000354	51,020
24.5×10^{-6}	0.077	0.000262	40,816
29.4×10^{-6}	0.109	0.000185	34,013

λ_{max} = 742.0 nm; concentration of diamide, **9** = 2.02×10^{-5} M. *K*a = 3.25×10^{3} M^{-1}; ε = 4.93×10^{4} [$M^{-1}cm^{-1}$] and r = 0.9951.

7.58–7.60 (m, 2H), 7.37–7.43 (m, 6H), 7.33–7.35 (m, 4H), 7.30–7.32 (m, 4H), 7.25–7.28 (m, 2H), 7.11–7.16 (m, 4H), 6.94 (d, 2H, *J* = 8 Hz), 4.80 (ABq, 4H *J* = 11.3 Hz, C$\underline{H_2}$O), 4.41 (d, 4H, *J* = 5.8 Hz, C$\underline{H_2}$N); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.8, 162.4, 159.9, 158.1, 139.5, 135.8, 135.7, 135.6, 134.2, 129.8, 129.4, 129.2, 129.2, 127.9, 127.9, 119.6, 117.6, 115.1, 114.9, 113.2, 67.8, 41.9; MS (ES) *m*/*z*: 669.2 $[M+H]^+$; Elemental Anal. Calc. for. $C_{42}H_{34}F_2N_2O_4$: C, 75.43; H, 5.12; N, 4.19%]; Found: C, 75.12; H, 5.25; N, 4.31%.

*2.3.13. 3,3′-(biphenyl-2,2′-diylbis(methylene))bis(oxy)bis(N-(4-methylbenzyl)benzamide) (**13**)*

Yield 78%; mp 78 °C; IR (KBr, cm^{-1}) 1640; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.93 (t, 2H, *J* = 5.9 Hz, N$\underline{H}$), 7.57 (d, 2H, *J* = 7.0 Hz), 7.34–7.43 (m, 8H), 7.27–7.30 (m, 4H), 7.17–7.19 (m, 4H), 7.10–7.12 (m, 4H), 6.93 (d, 2H, *J* = 8.2 Hz), 4.80 (ABq, 4H *J* = 11.4 Hz, C$\underline{H_2}$O), 4.38 (d, 4H, *J* = 5.9 Hz, C$\underline{H_2}$N), 2.26 (s, 6H, C$\underline{H_3}$); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.7, 158.1, 139.5, 136.6, 135.8, 134.3, 129.8, 129.4, 129.2, 128.8, 127.9, 127.8, 127.2, 119.6, 117.6, 113.2, 67.8, 42.4, 20.7; MS (ES) *m*/*z*: 661.3 $[M+H]^+$; Elemental Anal. Calc. for. $C_{44}H_{40}N_2O_4$: C, 79.97; H, 6.10; N, 4.24%; Found: C, 79.52; H, 5.59; N, 4.39%.

*2.3.14. 3,3′-(biphenyl-2,2′-diylbis(methylene))bis(oxy)bis(N-(4-methoxybenzyl)benzamide) (**14**)*

Yield 62%; mp 198 °C; IR (KBr, cm^{-1}) 1640; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.92 (t, 2H *J* = 5.9 Hz, N$\underline{H}$), 8.58–8.60 (m, 2H), 7.37–7.43 (m, 6H), 7.34–7.36 (m, 2H), 7.25–7.30 (m, 4H), 7.21 (d, 4H, *J* = 8.6 Hz), 6.93(d, 2H, *J* = 8.0 Hz), 6.86 (d, 4H, *J* = 8.6 Hz), 4.80 (ABq, 4H *J* = 11.4 Hz, C$\underline{H_2}$O), 4.37 (d, 4H, *J* = 5.9 Hz, C$\underline{H_2}$N), 3.87 (s, 6H, C$\underline{H_3}$O); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.7, 158.2, 158.1, 139.5, 135.8, 134.3, 131.6, 129.8, 129.4, 129.2, 128.6, 127.9, 127.9, 119.6, 117.6, 113.7, 113.2, 67.8, 55.1, 42.1; MS (ES) *m*/*z*: 693.2 $[M+H]^+$; Elemental Anal. Calc. for. $C_{44}H_{40}N_2O_6$: C, 76.28; H, 5.82; N, 4.04%; Found: C, 76.12; H, 5.59; N, 4.31%.

3. Results and discussion

3.1. Chemistry

The synthetic pathway leading to diamides **1**–**7** is outlined in Scheme 1. Reaction of *bis*-oxycarboxylic acid **15** (Rajakumar et al., 2012) with corresponding amines in the presence of

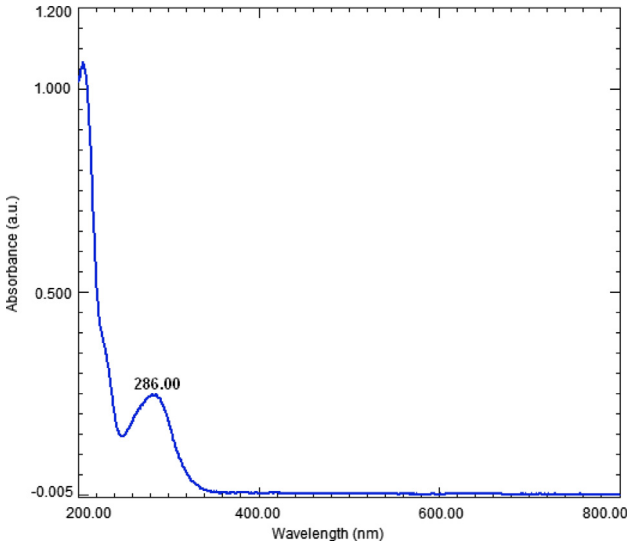


Figure 2b UV spectrum of diamide **9**.

(*O*-Benzotriazole-*N*,*N*,*N*′,*N*′-tetramethyl-uronium-hexafluorophosphate) HBTU in dry DMF at room temperature afforded the amides **1**–**7** in about 65, 60, 70, 65, 68, 75 and 72% yields, respectively. The ^{1}H NMR spectrum of diamide **1** displayed the *O*-methylene protons as a singlet at δ 4.68 and NH protons as a singlet at δ 9.65. The rest of the aromatic protons appeared between δ 7.04 and 7.48. In the ^{13}C NMR spectrum of **1**, the *O*-methylene carbons appeared at δ 67.7 and carbonyl carbon at δ 166.6. The FT–IR spectrum of **1** showed the carbonyl carbon stretching frequency at 1683 cm^{-1} and the mass spectrum showed the molecular ion peak ($[M+H]^+$) at m/z 453.1. Similarly the structures of diamides 2–7 were confirmed from spectral and analytical data. All the new compounds gave satisfactory FT–IR, ^{1}H and ^{13}C NMR, mass spectral and elemental analysis.

The synthetic pathway leading to diamides **8**–**14** is outlined in Scheme 2. Reaction of *bis*-oxycarboxylic acid **16** (Rajakumar et al., 2012) with corresponding amine **17**–**23** in the presence of HBTU in dry DMF at room temperature afforded the amides **8**–**14** in about 65, 70, 65, 65, 66, 74 and 62% yields, respectively. The ^{1}H NMR spectrum of diamide **8** displayed the *O*-methylene protons as an AB quartet at δ 4.86 and NH protons as a singlet at δ 10.18. The rest of the aromatic protons appeared between δ 7.02 and 7.74. In the ^{13}C NMR spectrum of **8**, the *O*-methylene carbons appeared at δ 67.8 and carbonyl carbon at δ 165.1. The FT–IR spectrum of **8** showed the carbonyl carbon stretching frequency at 1652 cm^{-1} and the mass spectrum showed the molecular ion peak ($[M+H]^+$) at m/z 605.2. Similarly the structures of diamides **9**–**14** were confirmed from spectral and analytical data. All the new compounds gave satisfactory FT–IR, ^{1}H and ^{13}C NMR, mass spectral and elemental analysis.

The amide **9** was recrystallized from acetonitrile. XRD studies indicate that intermolecular hydrogen bonding exists in amide **9**. In the crystal structure, the two benzene rings of the biphenyl unit form a dihedral angle of 114.06 (17). The tilt can be related to non-planarity geometry of the amide compounds (Saeed et al., 2012). Interestingly in the diamide **9** the two terminal 4-chloroaniline moieties attached to 3,3′-(biphenyl-2,2′-diyl*bis*(methylene))*bis*(-oxy)-dibenzoic acid

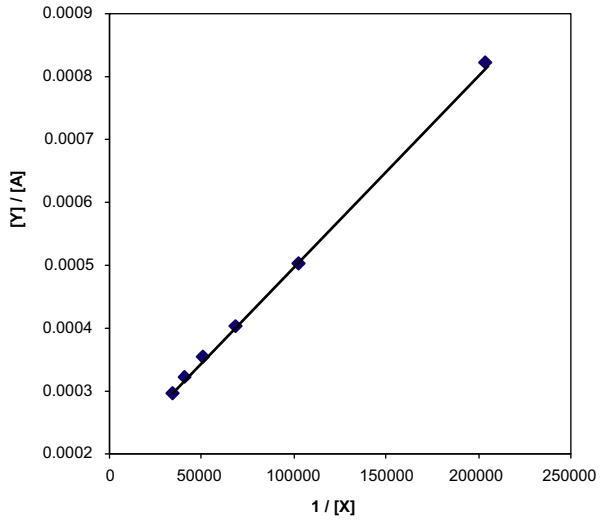


Figure 3 Plot between 1/X and Y/A for diamide **9**.

experience a static disorder over two positions. The refined site occupancies of the major and minor component for moiety-I are 0.657 (15):0.343 (15) and for the moiety-II are 0.509 (13):0.491 (13). The centro symmetric related molecules are linked through two N—H···O hydrogen bonds. N2—H2A···O1^{i} and N1—H1···O4^{ii} [Symmetry codes: (i) $-x + 1$, $-y + 1$, $-z + 1$; (ii) $-x$, $-y + 1$, $-z + 1$] to form two $R_2^2(38)$ ring motif. These rings are fused together to from infinite molecular ribbon networks extending along [100] direction. The crystal parameters for amide **9** are given in Table 1 and ORTEP diagram is shown in Fig. 1.

3.2. Complexation studies

Diamides **1–14** form charge transfer complexes with 7,7,8,8-tetracyanoquinodimethane (TCNQ) (Benesi and Hildebrand, 1949). Complexation studies of compounds **1–14** with tetracyanoethylene (TCNE) and paraquat (PQT) were not successful. Diamides **1–14** show UV–Vis absorption maxima at 240.0, 247.0, 248.0, 275.5, 232.0, 272.0, 276.0, 264.0, 286.0, 286, 287.0, 271.0, 267.0 and 275.0 nm respectively. However, the acceptor TCNQ shows an absorption maximum at 395.0 nm. Diamides, **1–14** form a charge transfer complex with TCNQ as evidenced by the appearance of absorption maxima at 742.0, 742.0, 742.0, 742.0, 742.0, 743.0, 743, 742.0, 743.0, 744.0, 742.0, 744.0, 743.0 and 743.0 nm respectively (Table 2 and Fig. 2a). The studies were carried out as outlined below. A solution of TCNQ (4.9×10^{-6} M) in a 1:1 mixture of $CHCl_3$/CH_3CN was prepared and (1 mL, 2 mL, 3 mL, 4 mL, 5 mL and 6 mL) added to the solution of the diamide (2.34×10^{-5} M) in a 1:1 mixture of $CHCl_3$/CH_3CN (3 mL) in a quartz cuvette of path length 1 cm. The UV–Vis spectrum was also obtained for each of the sample separately and the changes in the absorbance of CT bands were recorded.

The CT complexation study of **9** with various concentrations of TCNQ is shown in Table 3. The plot of (concentration of amide)/absorbance (Y/A) vs 1/concentration of guest (1/X) was linear (Fig. 2b). Benesi–Hildebrand equation was employed to calculate Ka (association constant) values. From the slope and the intercept values, K_a (K_a = intercept × slope^{-1}) and ε (ε = intercept^{-1}) were evaluated. The plot was linear suggesting that the predominant species in solution as a 1:1 complex (Fig. 3). The *K*a, ε and *r* values of the CT complexes formed from **1–14** with TCNQ are shown in Table 4. All the compounds showed above effectively form charge transfer complexes with TCNQ. Amide **7**, **3**, **6**, **4** and **1** bind TCNQ more strongly than **5** and **2** in the *bis*-phenoxy derivative. Similarly amide **14**, **10**, **13**, **11** and **8** bind TCNQ more strongly than **12** and **9** in the biphenyl carbinol derivative. This indicates that the electron donating substituent like methoxy and methyl groups enhances the binding of TCNQ with amide, whereas the electron withdrawing substituent like fluoro and chloro groups decreases the binding of TCNQ with amide. Complexation studies of **1–14** with tetracyanoethylene (TCNE) and paraquat (PQT) were not successful.

Table 4 Complexation of TCNQ with diamides **1–14**.

Amide	*K*a (mol^{-1}dm^3)	ε [M^{-1}cm^{-1}]	*r*
1	1.18×10^4	1.35×10^4	0.9950
2	9.08×10^2	2.21×10^5	0.9992
3	6.35×10^4	5.13×10^3	0.9998
4	2.58×10^4	1.52×10^4	0.9980
5	1.11×10^3	1.08×10^5	0.9916
6	1.12×10^4	9.77×10^3	0.9965
7	3.36×10^4	7.38×10^3	0.9983
8	1.49×10^4	1.25×10^4	0.996
9	3.25×10^3	6.47×10^4	0.9951
10	3.88×10^4	5.07×10^3	0.9983
11	3.35×10^4	1.13×10^4	0.9986
12	1.90×10^3	1.03×10^5	0.9985
13	3.06×10^4	1.13×10^4	0.9984
14	8.06×10^4	7.28×10^3	0.9993

4. Conclusions

In summary, we have synthesized various *bis*-oxy diamides with different substituents:

- In crystal structure of diamide 9, the two terminals of *p*-chloroaniline moieties attached to the *bis*-oxy acid experience a static disorder over two positions.
- In Charge transfer complexation studies, diamide with electron donating substituent like methoxy and methyl groups binds TCNQ more strongly than the electron withdrawing substituent like fluoro and chloro groups.

Supplementary material

Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 890615. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [e-mail: deposit@ccdc.cam.ac.uk].

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